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Standard Test Methods for Rubber Deterioration—Reference and Alternative Method(s) for Determining Ozone Level in Laboratory Test Chambers[1]

This standard is issued under the fixed designation D 4575; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

Numerous techniques exist for the analysis of gaseous ozone in ozone-air mixtures used for ozone crack testing of rubber. These include wet chemical procedures, electrochemical cells, UV absorption, and chemiluminescence with ethylene. See Refs (**1-4**).[2]

Wet chemical methods (the absorption of ozone in a potassium iodide solution and titration of the iodine released with sodium thiosulfate) have been in traditional use in the rubber industry, but they are not suitable for continuous operation, and in recent years they have been shown to be sensitive to small variations in test procedures and concentration and purity of reagents. Interlaboratory tests have indicated that different procedures do not give equivalent results, and most of them differ from an absolute UV method. Frequently, wet chemical methods yield higher ozone concentrations due to the oxidizing capacity of other components of the ozone-air mixture.

Certain nonreference instrumental methods are amenable to automatic operation and for this reason they are included in this standard. They may be used for routine testing once calibrated against the reference UV method.

UV absorption is adopted as the reference method against which the others shall be calibrated. It is an absolute test method and is in common use by environmental protection agencies for the determination of pollutant ozone in air (see 2.3).

Although these test methods are concerned with ozone analysis, it also draws attention to the influence of atmospheric pressure on the rate of cracking of rubber at constant ozone concentration as normally expressed in terms of parts by volume. As described in Appendix X2, the variation in ozone resistance that can result between laboratories operating at significantly different atmospheric pressures can be eliminated by specifying ozone concentration in terms of the partial pressure of ozone.

1. Scope

1.1 These test methods cover the following three types of methods for the determination of ozone content in laboratory test chambers. Method A (UV absorption) is specified for reference or referee purposes and as a means of calibration for the alternative methods; Method B, instrumental device (electrochemical or chemiluminescence); and Method C, wet chemical techniques (see Appendix X1). These methods are primarily intended for use with tests for determining rubber ozone cracking resistance and thus are applicable over the ozone level range from 25 to 200 mPa.

NOTE 1—Prior to 1978, ozone concentrations were expressed in ASTM D11 Standards in parts per hundred million (pphm) of air by volume. See Appendix X2 for an explanation of the change to partial pressure in millipascals (mPa).

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For a specific hazard statement, see Note 2 and 5.1.*

[1] These test methods are under the jurisdiction of ASTM Committee D11 on Rubber and are the direct responsibility of Subcommittee D11.15 on Degradation Tests.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

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NOTE 2—**Warning—Ozone is a hazardous chemical.**

2. Referenced Documents

2.1 *ASTM Standards:* [3]

D 518 Test Method for Rubber Deterioration—Surface Cracking

D 1149 Test Method for Rubber Deterioration—Surface Ozone Cracking in a Chamber

D 1171 Test Method for Rubber Deterioration—Surface Ozone Cracking Outdoors or Chamber (Triangular Specimens)

D 3395 Test Methods for Rubber Deterioration—Dynamic Ozone Cracking in a Chamber

2.2 *ISO Standard:*[4]

ISO-1431/I, II and III Rubber Ozone Testing; Static, Dynamic and Analysis Methods (respectively)

2.3 *Federal Standard:*[5]

Code of Federal Regulations (Protection of Environment) Title 40 Parts 1 to 51, July 1, 1984, Appendix D (Ozone in Atmosphere) pp. 550–562

3. Summary of Methods

3.1 This standard includes the following three types of independent methods.

3.1.1 *Method A Reference Method (UV Instrument)*—For UV absorption instruments, the ozonized air is passed through a flow cell. UV energy (wavelength 254 nm) passes through the cell and the resultant energy is detected at the other end. The degree of absorption is dependent on the number of ozone molecules in the path. The absorption is compared to the absorption with zero ozone and the difference in energy received at the detector is converted into an electrical output and measured. See Appendix X2 for more details and information.

3.1.2 *Method B—Secondary Method (Instrumental Devices)*:

3.1.2.1 For chemiluminescent instruments, the ozonized air is passed through an analysis chamber, it contacts a stream of ethylene and the two gases undergo a chemiluminescent reaction with the emission of photons at about 430 nm. This emission is measured on a photomultiplier and converted to an electrical output.

3.1.2.2 For electrochemical methods, the ozonized air is bubbled at a fixed rate through a coulometric (Pt-Hg) cell containing a buffered solution of potassium iodide. The iodine liberated from the solution is ionized at the cathode and is transported to the anode by turbulence. At the anode, insoluble HgI is formed with the release of ionic charges equivalent to the ozone content of the O_3-air stream.

3.1.3 *Method C—Secondary Method (Wet Chemical Technique)*:

3.1.3.1 *Procedure C-1*—An ozonized air sample is passed through an efficient absorption device containing an aqueous buffered solution of KI. After a fixed absorption time, the I_2 released is titrated with $Na_2S_2O_3$ and the ozone concentration is calculated from the thiosulfate consumed.

3.1.3.2 *Procedure C-2*—An air sample is passed through a solution in an efficient absorption container with an electrode end point device. The solution contains buffered KI and an amount of sodium thiosulfate to permit exhaustive absorption in 20 to 30 min (total consumption of the sodium thiosulfate). At the endpoint, the voltage across the electrodes abruptly increases and the time of this increase is recorded. The time is related inversely to the ozone content.

4. Significance and Use

4.1 General purpose and many specialty rubbers will undergo ozone cracking when exposed to ozone containing atmospheres, when the test specimens or actual use products are under a certain degree of tensile strain. Certain additives such as antiozonants and waxes inhibit or prevent this cracking. Various rubbers and rubber formulations containing such additives are customarily evaluated under static or dynamic tensile strain in laboratory ozone chambers. This standard provides for an accurate assessment of the ozone content of such chambers used in Test Methods D 518, D 1149, D 1171, D 3395 and ISO Standard 1431 I/II/III. For additional information on ozone analysis, refer to Code of Federal Regulations; Title 40 Parts 1 to 51.

5. Hazards

5.1 **Warning**—Ozone is a hazardous substance. Consult and follow all applicable laws, rules, and regulations regarding exposure to ozone.

6. Calibration of Nonreference Methods

6.1 The secondary (sec) methods shall be calibrated with respect to one of two reference ozone systems;

6.1.1 *Reference O_3 System No. 1*, consisting of (*1*) stable O_3 generator with adjustable output in the range from 0 to 500 mPa and (*2*) a reference UV ozone analyzer (Method A type).

6.1.2 *Reference O_3 System No. 2*, consisting of a UV photometric O_3 calibration system (calibration O_3/air supply). This system generates reference levels of ozone, but it does not function as an analyzer. See Appendix X2 for more information.

6.2 *Apparatus Required for Reference O_3 System No. 1*:

6.2.1 *Adjustable Level*, stable, generator of ozonized air. This is normally a UV lamp, flow rate, and containment system.

6.2.2 *System*, permitting the output from the ozone generator to be selectively switched to inputs for (*1*) the reference UV ozone measuring device and (*2*) the (secondary) ozone measuring device to be calibrated. The tubing for the ozonized air should be clean, PTFE or glass, and be as short as possible. A PTFE cock for switching is mandatory to prevent O_3 decomposition.

6.3 *Calibration Procedure*:

6.3.1 Select at least three (preferably five) ozone levels that span the range of interest. Select the lowest level and must be

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

[5] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

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generator. Allow it to become stable in output to within ±5 % variation for several measurements made in a short time span by monitoring the output ozone with the reference UV device. Record the average ozone level.

6.3.2 Switch the ozone output to the secondary ozone measuring device, and measure the ozone several times over a time period sufficient to get an average value with individual deviations no greater than ±5 %. Record the average ozone level measured with the secondary device.

6.3.3 Take care to execute 6.3.1 and 6.3.2 until the indicated repeatability (precision) of ±5 % is attained; this indicates stable output and good secondary measurement procedure.

6.3.4 Repeat the procedure of 6.3.1 and 6.3.2 for the other two (or four) levels in ascending order.

6.3.5 Plot the average concentrations, O_3(Sec) versus O_3(Ref), and determine linear regression parameters b_0 and b_1.

$$O_3(\text{Sec}) = b_0 + b_1 O_3\,(\text{Ref}) \quad (1)$$

$$O_3\,(\text{Ref}) = O_3(\text{Corr}) = \frac{O_3(\text{Sec}) - b_0}{b_1} \quad (2)$$

6.3.6 To obtain true or reference O_3 concentration in routine daily work, use Eq 2. The value as calculated from Eq 2 is called the corrected ozone concentration, O_3(corr).

6.3.7 The uncertainty of the corrected routine daily ozone level or concentration as calculated from Eq 2 will depend on the number of average values, reference and secondary, used in establishing the linear regression calibration line, upon the number of measurements forming each plotted average, and upon the basic measurement error of the secondary method. If five ozone levels are used to establish the linear regression line, an estimate of the standard deviation of the corrected ozone concentration (SD, O_3(corr)) that is, the standard error of the estimate, with three degrees of freedom, may be obtained by the use of Eq 3.

$$SD(O_3(\text{corr})) = \left(\frac{N-1}{N-2}(S_y^2 - b_1^2 S_x^2)\right)^{1/2} \quad (3)$$

where:

N = number of plotted points,
b_1 = slope of regression curve of Eq 1,
S_y^2 = variance among plotted (average) secondary method O_3 concentrations, and
S_x^2 = variance among plotted (average) reference method O_3 concentrations.

6.3.8 Thus the (±)90 % confidence limits on the corrected ozone concentrations are ±1.64 SD (O_3(corr)) for a linear regression curve obtained with 5 reference and secondary levels of ozone.

6.4 *Apparatus Required for Reference O_3 System No. 2*:

6.4.1 A UV photometric ozone calibration system shall be used. Various commercial systems may be used provided they indicate ozone concentration to the same accuracy and precision as specified in 8.2 for the direct reading UV ozone analyzer.

6.5 *Calibration Procedure*:

6.5.1 Follow the general procedure as outlined in 6.3. The procedure with the No. 2 Reference System varies from the No. 1 system only in the sense that the ozone generation and reference analysis are conducted in a self-contained system.

TEST METHOD A

7. Sampling

7.1 The sampling line shall be polytetrafluoroethylene (PTFE), or glass, or PTFE-lined material, or any other demonstrably unreactive and impermeable material. The line shall be as short as practicable and, unless otherwise specified, shall be no longer than 1 m in length. The line shall be designed so as to prevent ingress of contaminants. The combination of length and bore of the sampling line should be such as to minimize residence time of the sample without producing undue pressure drop.

8. Preparation of Apparatus

8.1 A direct-reading UV ozone analyzer or instrument shall be used.

8.2 When the instrument is used over the 0 to 500-mPa range, the parameters shall conform to the performance requirements given in Table 1.

8.3 *Initial UV Instrument Calibration*—The calibration procedure shall be as follows:

8.3.1 Set up the instrument in accordance with the manufacturer's instructions and allow a sufficient stabilization period. Set the instrument zero using zero air produced by suitably removing contaminants with a calibration O_3/air supply (see X2.1). Feed the zero air directly to the instrument and adjust the zero control after allowing sufficient stabilization time. See Table 1.

8.3.2 Span the instrument measuring circuit using a self-contained calibration atmosphere system as described in 6.1.1. See also X2.2.

8.3.3 Use three to five concentrations corresponding to the spread over the measuring range. Steady indicated values shall agree to within 2 % of the calibration value.

8.4 *Operational Recalibration*—The following procedure shall be carried out ideally on a daily basis, but at least weekly:

8.4.1 Check the instrument ozone level using zero air and take appropriate action, if necessary.

TABLE 1 Performance Requirements for UV Instruments Used in the Determination of Ozone in Ambient Air

Parameter	Requirements
Range	0 to 500 mPa
Noise	0.5 mPa
Lower detectable limit	1.0 mPa
Interference equivalent:	
Each interferent	±2 mPa
Total interferent	±6 mPa
Zero drift, 12 h and 24 h	±2 mPa
Span drift, 24 h	
20 % of upper range limit	±20.0 %, max
80 % of upper range limit	±5.0 %, max
Lag time	2 min, max
Rise time	2 min, max
Fall time	2 min, max
Precision:	
20 % of upper range limit	1.0 mPa, max
80 % of upper range limit	1.5 mPa, max

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